

# Reactions of Uranium With the Platinide Elements.

## I. The Uranium-Ruthenium System\*

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(August 12, 1967)

The phase diagram of the uranium-ruthenium system was constructed from data obtained by thermal analysis, metallographic examination, and x-ray diffraction. The system is characterized by five intermetallic compounds:  $U_2Ru$ , formed peritectically near 937 °C; "URu," melting congruently near 1158 °C;  $U_3Ru_4$ , formed peritectically near 1163 °C;  $U_3Ru_5$ , formed peritectically near 1182 °C; and  $URu_3$ , formed peritectically at about 1850 °C. "URu" has a solid-state transition at about 795 °C. One eutectic occurs near 886 °C and 18.5 atomic percent (a/o) ruthenium, and a second at about 1148 °C and 49 a/o ruthenium. The maximum solid solubilities are about 7.5 a/o ruthenium in uranium and near 1.3 a/o uranium in ruthenium. Ruthenium lowers the gamma-uranium transformation to near 691 °C and the beta-transformation to near 625 °C.

Key Words: Phase diagram, intermetallic compound, ruthenium, solubility, uranium.

### 1. Introduction

This report on the uranium-ruthenium system was conducted for the Atomic Energy Commission and is one of a series of investigations of the reactions between uranium and the individual elements of the platinide metals in Group VIII of the periodic chart. In addition to determining the equilibrium diagrams, an attempt was made to determine some theoretical basis for metallic reactions. These binary phase diagram studies have resulted in a correlation among solid solubility, atomic radius, and the crystal lattice of the solvent, which will be presented in the final report of this series. Thermal analysis, metallographic examination, and x-ray diffraction data were combined to produce this proposed phase diagram.

### 2. Previous Work

The compilation of the constitution diagrams of uranium and thorium alloys by Rough and Bauer [1]<sup>1</sup> summarized the known data on the reactions of uranium with the other elements, including the platinide elements. The uranium-ruthenium diagram was incomplete and contained some information contributed from this study. The compilation by Hansen and Anderko [2] mentioned only the crystal structure of

the  $URu_3$  compound. Additional information on the reactions of uranium with ruthenium could be found in various reports from the Argonne National Laboratory Metallurgy Division, though these were summaries only [3, 4, 5]. A partial diagram appears in the compilation by Elliott [6] and presented previously by Chiswick [7] which was gathered from Argonne National Laboratory data. That summary showed the existence of six compounds and additional information which is at variance with the results reported here. The complete diagram with supporting data has apparently not yet been published.

### 3. Preparation and Analysis of Alloys

The uranium utilized in the making of the alloys was of about 99.9 percent purity (Mallinckrodt biscuit). The ruthenium was obtained as powder of about 99.9 percent purity. Qualitative spectrochemical analysis of this material by E. K. Hubbard at NBS indicated that the ruthenium contained only small amounts of palladium, platinum, and rhodium among the metallic impurities. The estimated impurity content is as follows: 0.01–0.1 percent Fe, Pd; 0.001–0.01 percent Al, Cu, Mg, Mn, Ni, Pb, Pt, Rh, Si; and 0.0001–0.001 percent Ag, Ca.

The uranium was sliced into sections of appropriate size to produce alloys of 50 to 100 g. The ruthenium powder was compressed into pellets 1/4 in in diameter as a preparatory step. Alloys of up to 70 atomic percent (a/o) ruthenium had been made by vacuum induc-

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<sup>1</sup>Figures in brackets indicate the literature references at the end of this paper.

tion melting in a beryllia crucible; these showed no alloy-crucible reaction. Additional alloys of from 33 to 100 a/o ruthenium content were made by arc-melting under a helium atmosphere on a water-cooled copper hearth using a tungsten electrode; these alloys were remelted to ensure complete alloying.

Confirmatory chemical determinations of one or of both constituents were made by J. R. Baldwin and E. J. Maienthal in the Analytical Chemistry Division, NBS, on some of the "as melted" alloys and sometimes on the "thermal analysis" or homogenized samples. The ruthenium content for alloys of less than 13 atomic percent (a/o) was determined colorimetrically, and for alloys of higher ruthenium content a gravimetric method was used. The uranium determinations were made colorimetrically for alloys of less than 15 a/o uranium and a volumetric method was used for alloys of greater than 15 a/o. The difference between the nominal and analyzed compositions was small, being less than 1.0 a/o. The atomic percentages of the alloys were calculated on the basis of the analyses, and these percentages are used when discussing the results of the experiments.

## **4. Procedures**

### **4.1. Metallography**

Specimens were mounted in thermosetting plastic material and then rough ground on a series of silicon carbide papers, the final paper being 600 grit. The samples were polished on lubricated broadcloth laps with successively finer diamond particles, nominal  $1/4 \mu$  powder being the last.

The uranium-rich alloys were electroetched in a solution of 5 parts orthophosphoric acid, 8 parts ethylene glycol, and 8 parts ethyl alcohol, with a power input of about 30 V dc and 10 A/cm<sup>2</sup>. An additional electrolytic etch for uranium-rich alloys was a 10 percent chromic acid solution at 5 V dc and 1 A/cm<sup>2</sup>. Alloys in the range of 20 to 80 percent ruthenium were etched by immersion in a 60 percent nitric acid solution or by an electrolytic etch with 60 percent perchloric acid in water at 10 V dc and 1 A/cm<sup>2</sup>. The ruthenium-rich alloys, particularly near the single-phase regions, were etched in a 5 percent sodium cyanide solution at 10 V ac and 10 A/cm<sup>2</sup>.

### **4.2. Thermal Analysis**

Approximately 50 g of as-melted alloy was loaded into a thermal analysis furnace [8] for determination of the respective reaction temperatures. The thermal analysis data were derived from recordings of time versus temperature as the samples went through a heating and cooling cycle. The thermal analysis furnace has a molybdenum wire resistance heating element and may be operated under vacuum or purified inert gas atmosphere. The peak temperature of the furnace is near 1600 °C.

An electronic controller is used for either manual or automatic control of the heating or cooling portions of the test. The power input of the furnace is changed through a motor-driven variac, the rate being selected by operation of a clock-interrupter which supplies power to a magnetic clutch in the gear train. A heating and cooling rate of approximately 3 °C/min was most frequently used, though different rates were occasionally selected when a particular feature of the curve was examined more closely.

The thermal analysis crucible had been prepared from beryllia powder by slip-casting. The crucible was made with a small "well" in the bottom into which the thermocouple tip could fit and be protected by the beryllia of the well. This type of crucible permitted the alloy to melt around the well and the inner thermocouple bead, thus providing rapid and accurate determination of reaction temperatures.

Temperature determinations were made with a Pt versus Pt-10 Rh thermocouple. The thermocouples were annealed and then calibrated against NBS standards. The thermocouples used in the quenching experiments were treated similarly and were also calibrated prior to use and were checked after a number of quenches. The thermal analysis thermocouples were calibrated prior to each use.

For high-temperature studies, a filament-furnace was used in which a thin, notched sample served as the filament and was heated by its own electrical resistance. Optical pyrometer temperature measurements were made as these samples were heated or were held at temperature; the samples could be quenched by turning off the power. An induction furnace was utilized for heating some specimens; this furnace consisted of a quartz tube 3 inches in diameter, which could be evacuated by means of a mechanical pump and an oil diffusion pump. The power was supplied by a 20 kW induction generator; the smaller specimens were heated by radiation from a molybdenum or graphite susceptor. These specimens were contained in a beryllia or magnesia crucible and could be held at temperatures for extended times with little apparent temperature fluctuation.

### **4.3. X-Ray Analysis**

X-ray diffraction patterns were obtained from many of the metallographic specimens in the polished or etched conditions. The radiation employed was that from copper or cobalt targets and filtered to eliminate the K-beta radiation. Recordings of the diffraction peaks were converted to lattice spacings for identification and comparison of the respective patterns. Film techniques were also frequently employed. Powder cameras with diameters of 57.3 and of 114.6 mm were used, and corrections for film shrinkage were made.

### **4.4. Heat Treatment**

Portions of each alloy were taken for homogenization treatment. The homogenization was conducted in a tube-type resistance furnace with the samples sealed

in high-silica glass tubing under a helium atmosphere as protection against oxidation. The capsules containing the alloys were loaded into a ceramic boat and inserted in the hot furnace; the boat rested at a point less than 1/4 in from the control thermocouple and a calibrated indicating thermocouple. The samples were at a temperature selected from thermal analysis data and were equilibrated for about 200 hr. The boat was then removed from the furnace and the samples cooled in circulating air.

Individual specimens were cut from the homogenized bar, and these were sealed individually in small silica capsules. For quenching, the samples were heated in a resistance-wound furnace; the furnace was made by winding 40 mil platinum wire on a 1 in i.d. alundum tube and surrounding it with insulation. The maximum temperature of this furnace was over 1350 °C. The individual specimens were wired to the underside of the quenching block [9], so designed that the protective silica tubing was certain to break against the bottom of the ice pot on quenching and permit rapid quenching. The indicating thermocouple was resting against one end of the sealed silica tubing and was removed just prior to quench. The temperature was determined frequently and the power input to the furnace was hand-adjusted to approach the desired temperature at a rate of about 1 °C/min for the last half hour. The thermocouple was calibrated before a number of quenches and was checked again after a series of quenches so that appropriate corrections could be made to the indicated temperature.

## 5. Results

### 5.1. The Region of 0 to 35 a/o Ruthenium

The addition of ruthenium to uranium has a considerable effect upon the melting point and the transformation temperatures of uranium. The thermal analysis results are shown in table 1 and are plotted in figure 1. The data were obtained for alloys cooled at 3 °C/min.

TABLE 1. Thermal analysis results, U-Ru

Alloys of 0-35 a/o ruthenium

Reactions °C					
a/o Ru	Fusion	Eutectic	Arrest	$\gamma \rightarrow \beta$	$\beta \rightarrow \alpha$
0	1131			767	657
1.1	1110			724	624
4.2	1068			686	627
5.0	1056			689	624
6.8	1032			697	638
14.0	938	883		696	619
20.9	904	890		691	616
27.4	934	885		687	
34.7	936		774		

Small percentages of ruthenium produce a considerably lower melting point for the alloys as compared to that for unalloyed uranium. The 5.0 a/o ruthenium alloy has a freezing point of 1056 °C, a reduction of 75 °C. The trend of the freezing points of the alloys

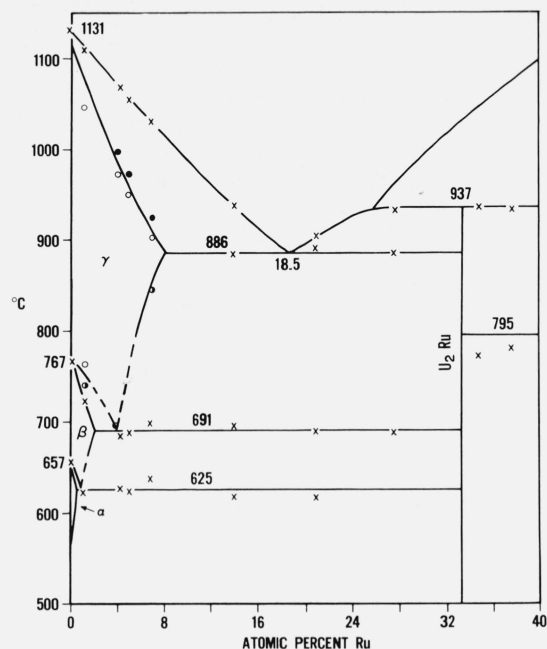


FIGURE 1. Uranium end of U-Ru system.

indicate the existence of a eutectic at about 886 °C and very near 18.5 a/o ruthenium. The addition of ruthenium also lowers the transformation temperatures of uranium. The 5.0 a/o ruthenium alloy has its gamma-beta reaction at 689 °C, a depression of 78 °C, while its beta-alpha reaction occurred at 624 °C, a depression of 33°. The gamma-beta reaction is stabilized at an average of 691 °C for alloys in the range of 4.2 to 27.4 a/o ruthenium. The beta-alpha uranium reaction is at about 625 °C, and it could be detected near this temperature in alloys containing from 1.1 to 20.9 a/o ruthenium. As the ruthenium content approached 33 a/o the uranium transformations were less apparent, with only the gamma-beta reaction being detected in the thermal analysis chart for the 27.4 a/o alloy.

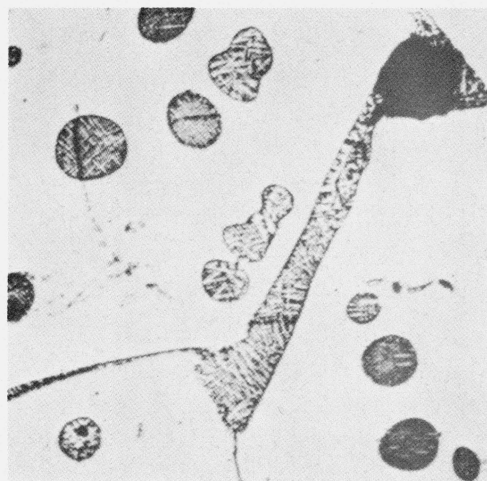
The first intermetallic compound adjacent to the terminal uranium solid solution fields is located at 33.3 a/o ruthenium, U<sub>2</sub>Ru. The metallographic appearance of the alloys of low ruthenium content and the detection of the uranium transformations up to 27.4 a/o ruthenium by thermal analysis indicate that there is no compound of less than 33.3 a/o ruthenium. The U<sub>2</sub>Ru phase is formed by a peritectic reaction near 935 °C, as indicated by thermal analysis results and confirmed by quenching experiments. As further evidence, Berndt [10] has reported that the U<sub>2</sub>Ru phase has the monoclinic lattice.

### 5.2. The Solid Solubility of Ruthenium in Uranium

Alloys containing up to 6.8 a/o ruthenium were quenched at selected temperatures to determine the extent of the ruthenium solid solubility in the terminal uranium phases; to determine by x-ray diffraction whether beta- or gamma-uranium could be retained

by quenching to room temperature; and, to detect the beginning of melting at the higher temperatures. For the determination of fusion the samples were quenched from the maximum temperatures attained. For the quenches from the beta- and alpha-uranium phase regions the samples were heated to about 825 °C and then cooled to the desired quench temperature. Portions of the alloys had been homogenized at 825 °C for 8 days prior to being cut and sealed for quenching.

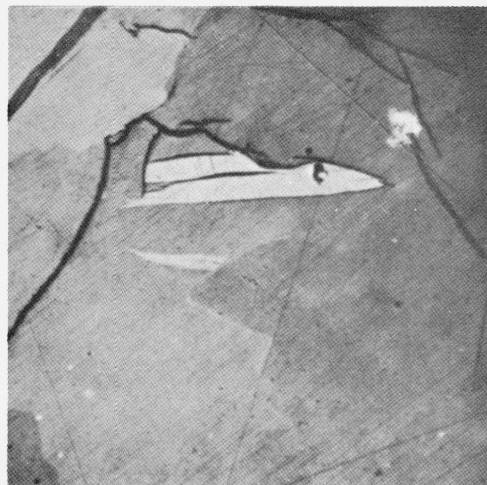
The solid solubility of ruthenium in both the alpha- and the beta-uranium structure is relatively low, as might be expected from a consideration of the complex nature of the uranium crystal structures. The thermal analysis data indicate that the beta-alpha reaction in the 1.1 a/o ruthenium alloy was at the minimum of 624 °C, thus indicating that the solubility of ruthenium in alpha-uranium is less than 1.1 a/o. The thermal analysis data for this 1.1 a/o ruthenium alloy show the



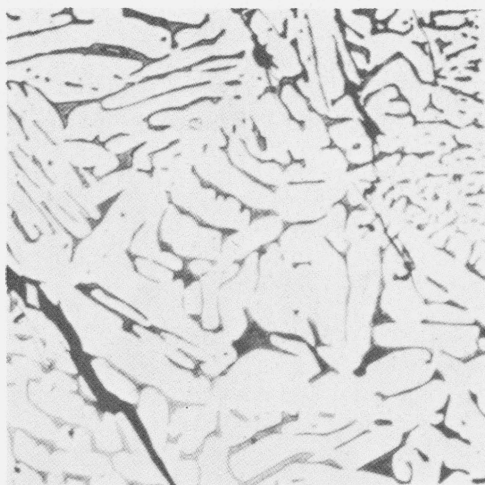
(a)



(b)



(c)



(d)

FIGURE 2. *Metallographic appearance of quenched specimens.*

- (a) Fusion in alloy of 4.2 a/o ruthenium, quenched from 1000 °C. Chromic acid etch.  $\times 100$ .
- (b) Single phase alloy of 5.0 a/o ruthenium, quenched from 630 °C. As electropolished.  $\times 100$ .
- (c) Single phase alloy of 1.1 a/o ruthenium, quenched from 757 °C. Polarized Light.  $\times 100$ .
- (d) Two phase alloy of 1.1 a/o ruthenium, quenched from 736 °C. Glycol etch.  $\times 100$ .



gamma-beta reaction completed at 724 °C, and extrapolation from 767 °C for the unalloyed uranium to 691 °C for alloys of 4.2 percent and higher ruthenium indicates that the solubility of ruthenium in beta-uranium is less than 2 a/o. The quenched specimens of 1.1 a/o ruthenium in the range of 600 to 736 °C were two phase with no indication of a single phase beta-uranium region; however, quench conditions are critical for retaining the beta-uranium phase. A difference in shape of the precipitate phase in the 1.1 a/o ruthenium alloy specimen indicated that it probably had been quenched from the alpha plus beta region. The specimen quenched from 760 °C for the same alloy was single phase, having been quenched from the gamma-uranium field; this alloy remained single phase when quenched from a maximum of 1050 °C.

The solubility of ruthenium in gamma-uranium is considerably higher than in alpha- or beta-uranium. A summary of the metallographic examination of the quenched specimens is listed in table 2 and some data are presented in figure 1. The sample of 6.8 a/o ruthenium showed decreasingly smaller amounts of a second phase as the quench temperature rose from 670 toward 900 °C, but the sample quenched from 903 °C was single phase, and fusion areas appeared above 927 °C. The maximum solubility of ruthenium in gamma-uranium is about 7.5 a/o, since the extension of the solvus and solidus lines places the terminal point under 8 a/o. The occurrence of fusion (fig. 2a) between 977 and 1000 °C in the 4.2 a/o ruthenium alloy and between 903 and 927 °C in the 6.8 a/o ruthenium alloy outlines the solidus; the change from two phase to single phase between 736 and 757 °C in the 1.1 a/o ruthenium alloy, between 670 and 690 °C in the 4.2 a/o ruthenium alloy, and between 850 and 903 °C in the 6.8 a/o ruthenium alloy serve to outline the gamma-uranium field. The 5.0 a/o ruthenium alloy was single phase when quenched from 630 °C (fig. 2b) and it gave the  $\alpha$ -uranium diffraction pattern, even though thermal analysis detected the  $\beta$ -to- $\alpha$  reaction at 689 °C.

TABLE 2. Summary of metallographic observations of quenched specimens

Ru content	Fusion	One phase	Two phase
1.1 a/o	.....	1050 to 757 °C	736 °C
4.2	1000 °C	977 to 690 °C	670 °C
4.5	980 °C	947 to 870 °C	685 °C
5.0	.....	930 to 630 °C	.....
6.8	927 °C	903 °C	850 °C

The x-ray diffraction pattern for each quenched specimen was obtained utilizing the specimen as prepared for metallographic examination. The possibility of retaining the higher temperature uranium structures by quenching is apparent because of the extensive solid solubility, although the transformations usually do occur. In the two-phase alloy of 1.1 a/o ruthenium quenched from 736 and 757 °C, (fig. 2c,d) the beta-uranium diffraction peaks were detected, although the *d*-spacings were shifted somewhat as

compared with the unalloyed values [11]. In no other specimens was the beta-uranium detected, but the study by Tangri et al. [11B], on the metastable phases in uranium alloys indicated that the beta phase could be transformed by polishing with a wet emery paper. The numerous specimens which were single phase after quenching from the gamma-uranium region had apparently transformed to alpha-uranium, because each gave the alpha-uranium diffraction pattern.

### 5.3. The Region of 34 to 75 a/o Ruthenium

Thermal analysis results for alloys in the range of 34 to 70 a/o ruthenium showed the existence of a number of apparent reaction horizontals, given in table 3 and plotted in figure 6.

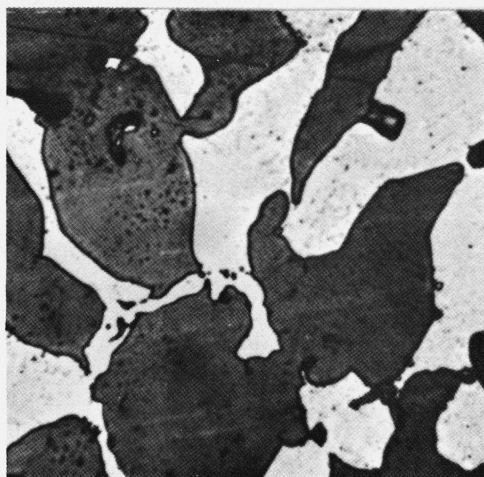
TABLE 3. Thermal analysis results, U-Ru  
Alloys of 34-70 a/o Ruthenium

Reactions °C					
a/o Ru	Fusion	Reaction	Eutectic	Peritectic	Reaction
34.7	.....	.....	.....	936	774
37.5	.....	.....	.....	934	782
43.6	1089	.....	.....	940	796
47.2	1158	.....	.....	.....	809
51.7	.....	.....	1147	.....	799
54.8	.....	1164	1147	.....	795
55.7	.....	.....	1149	.....	.....
57.0	.....	1166	.....	.....	.....
58.5	.....	1160	.....	.....	.....
61.6	.....	1173	.....	.....	.....
64.6	.....	1183	.....	.....	.....
69.7	.....	1181	.....	.....	.....
70.7	.....	1182	.....	.....	.....

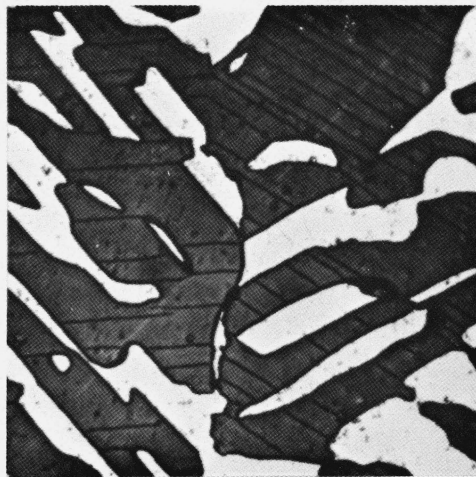
In the alloys of 27.5 to 43.6 a/o ruthenium a reaction consistently was found near 937 °C. As mentioned previously, this is the peritectic formation temperature of the  $U_2Ru$  compound. In alloys of 34.7 to 54.8 a/o ruthenium an additional reaction occurs at a lower temperature, very close to 800 °C. Additionally, in the region from 47 to 62 a/o ruthenium two more horizontal reactions were detected, at an average of 1148 and 1163 °C. A third reaction in this temperature region, near 1182 °C, was also detected in alloys of 61.6 to 70.7 a/o ruthenium. The presence of all of these horizontals indicates the existence of a number of intermetallic compounds.

The existence of the "URu" phase is apparent from metallographic examination. However, this phase seems to be formed of nonequal portions of uranium and ruthenium, for only at 47.2 a/o ruthenium was the single phase structure apparent. The melting point of this compound is at 1158 °C as determined by thermal analysis, while the horizontal located at 1148 °C is due to a eutectic reaction between "URu" and its next adjacent compound,  $U_3Ru_4$ . The existence of a eutectic is apparent in the alloys between these respective compositions, as in specimens quenched from 1140 °C.

The presence of the 795 °C reaction in the range of 34.7 to 54.8 a/o ruthenium was readily apparent in the thermal analysis charts. This arrest has been ascribed to a crystal structure transformation of the "URu"



(a)



(b)

FIGURE 3. Uranium-ruthenium of 36.7 a/o ruthenium.

(a) Alloy quenched from 790 °C. Perchloric acid electroetch  $\times 500$ .  
(b) Alloy quenched from 800 °C. Perchloric acid electroetch  $\times 500$ .

phase. To confirm this hypothesis a set of five alloys containing between 43.4 and 57.0 a/o ruthenium was heat treated at 890 °C for 70 hr and a second set at 780 °C for 75 hr. Though there was little difference in metallographic appearances due to the heat treatments (fig. 3), a comparison of the x-ray diffraction patterns of these sets of samples revealed that changes had occurred. The diffraction patterns for the high-temperature and the low-temperature structures of the "URu" compound are listed with the other diffraction data in table 4.

TABLE 4. X-ray diffraction data, interplanar spacings, U-Ru

$\alpha$ -U Ru (Quench-780 °C)		$\beta$ -U Ru (Quench-890 °C)		$U_3Ru_4$		$U_3Ru_5$	
<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>
2.87	vw	2.88	m	2.69	w	2.95	w
2.71	m	2.83	s	2.63	w	2.93	vw
2.48	m	2.61	m	2.52	m	2.84	w
2.43	m	2.53	w	2.48	m	2.78	s
2.37	w	2.47	s	2.35	s	2.70	m
2.31	s	2.21	vw	2.33	s	2.48	w
2.24	vw	2.13	vw	2.28	s	2.36	vw
2.11	s	1.94	vw	2.25	m	2.30	m
2.08	vw	1.84	w	2.04	w	2.28	m
1.80	vw	1.60	w	1.99	w	2.24	m
1.68	vw	1.46	vw	1.96	w	2.00	w
1.64	m	1.40	vw	1.90	w	1.86	vw
1.56	vw	1.30	vw	1.73	w	1.80	vw
1.37	w	1.26	vw	1.68	m	1.71	w
1.33	vw	1.25	w	1.62	w	1.66	s
1.27	vw	1.22	vw	1.59	w	1.61	vw
		1.19	vw	1.46	w	1.52	w
		1.16	vw	1.44	w	1.40	w
				1.40	vw	1.38	w
						1.31	w
						1.27	vw

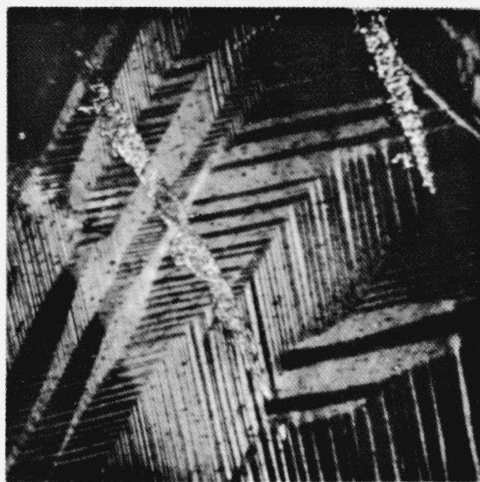
Data derived from diffraction patterns (charts) utilizing filtered Co or Cu radiation. Estimated relative intensities: s—strong; m—medium; w—weak; vw—very weak.

The presence of the reaction horizontal at an average of 1163 °C, as determined from thermal analysis of alloys in the range of 54.8 and 61.8 a/o ruthenium, is associated with the  $U_3Ru_4$  phase. This phase is ap-

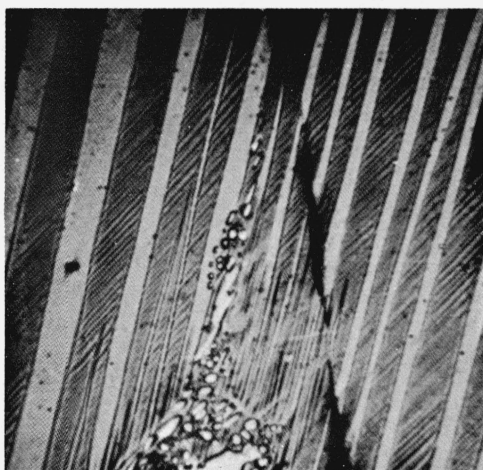
parently formed by a peritectic reaction, with 1163 °C being the reaction temperature. This phase is stable to room temperature. Of particular interest in detecting the existence of this phase is the appearance of a "banded" structure in alloys containing 51.7 to 58.5 a/o ruthenium. This structure was best observed with the interference microscope, with which obvious differences in depth were apparent (fig. 4). Attempts to obtain replicas for use on the electron microscope were unsuccessful due to the different sample levels.

The third reaction horizontal, occurring near 1182 °C, was detected in alloys of 61.6 to 70.7 a/o ruthenium, and it has been attributed to the peritectic reaction forming the  $U_3Ru_5$  phase. In this composition range, no arrest were noted at lower temperatures. Metallographic specimens, quenched from near this horizontal, remained solid up to 1170 °C while fusion of one phase occurred at temperatures above 1185 °C. The x-ray patterns of alloys in the 61.6 to 70.7 a/o ruthenium range confirmed the existence of a phase located at 62.5 a/o ruthenium,  $U_3Ru_5$ , and also revealed that it was adjacent to the  $URu_3$  phase. The results for this middle portion of the system are assembled in figure 5, and the x-ray data are given in table 4.

Some of the previous findings are at variance with the tentative results from Argonne National Laboratory personnel [12]; the latter source revealed a  $U_3Ru_5$  phase which was postulated to be stable above 870 °C but which decomposed below this temperature to the  $U_2Ru_3$  and  $URu_3$  phases. The  $U_2Ru_3$  phase was not found during this investigation. The absence of thermal reactions below 1100 °C in the 60 to 70 a/o ruthenium region in thermal analysis data of table 3 and the unchanging nature of alloys near 70 a/o ruthenium after heat treatments and quenching (fig. 5) strengthen the finding that the  $U_3Ru_5$  phase is stable from room temperature up to its peritectic decomposition temperature of 1182 °C.



(a)



(b)



(c)

FIGURE 4. *Banded structure of alloys near the  $U_3Ru_4$  phase.*

- (a) Sample of 54.8 a/o ruthenium after quench from 1060 °C. Etched.  $\times 350$ .  
 (b) Sample of 55.7 a/o ruthenium after quench from 1100 °C. Etched.  $\times 350$ .  
 (c) Interference micrograph picture of same area of sample of 55.7 a/o ruthenium after quench from 1100 °C.  $\times 350$ .

#### 5.4. The Region of 75 to 100 a/o Ruthenium

The first compound adjacent to ruthenium has the  $URu_3$  composition. Alloys in this composition range were sometimes heated by their own electrical resistance, as for an electric light filament, and measurements of the sample temperature made with an optical pyrometer; some samples were heated to elevated temperatures by induction heating. Specimens were usually held at temperature for 20 or 30 min, and it was observed that little fluctuation in the indicated temperatures occurred in either of these techniques.

The samples of high ruthenium content in the as-cast

condition contained dendrites; after 30 min at 1600 °C considerable grain growth had occurred and the dendrites had decomposed. In the temperature range of 1800 to 1900 °C an apparent reaction occurs; in the 91.8 a/o ruthenium alloy at 1800 °C the samples retained their square corners and at 1900 °C fusion had begun with a consequent change in microstructure. This reaction is apparently the peritectic decomposition of the  $URu_3$  compound, since the alloy of 75.5 a/o ruthenium is stable to a temperature between 1700 and 1900 °C and is also very close to being single phase.

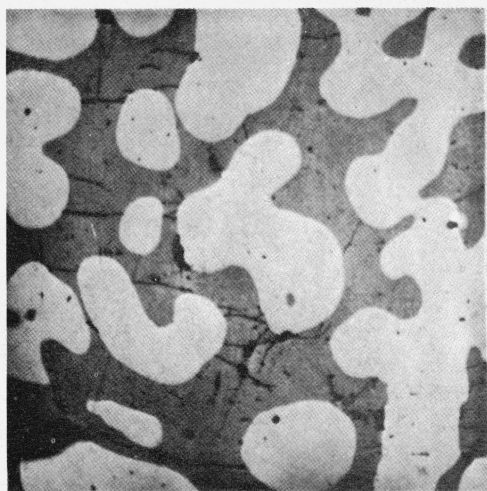
Each of the x-ray diffraction patterns of the alloys in the 75.5 to 96.3 a/o ruthenium range were mixtures of

the  $\text{URu}_3$  and the Ru patterns. No evidence of a compound between 75 and 100 a/o ruthenium was noted in any of the diffractometer charts; the powder patterns did give additional weak lines which were attributed to some oxidation of the powder samples. Thus it was concluded that the  $\text{URu}_3$  phase is the compound adjacent to the ruthenium end of the diagram, and it is formed by a peritectic reaction at about 1850 °C.

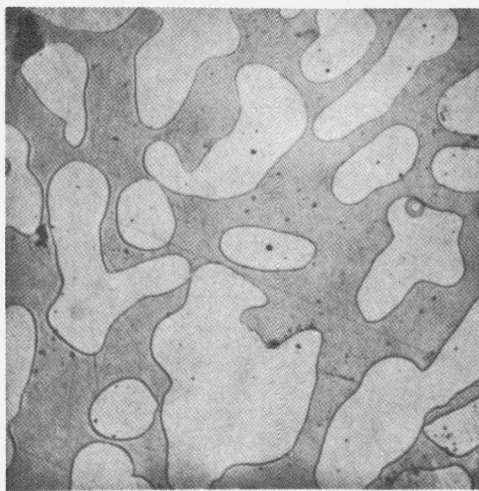
The  $\text{URu}_3$  compound has the cubic  $\text{Cu}_3\text{Au}$  structure, as reported by Heal and Williams [13]. The data obtained for this report are in agreement with the reported structure, and the relative intensities also matched well.

The solid solubility of uranium in ruthenium was determined by x-ray diffraction utilizing the diffractometer. Annealed silver powder was scattered on the metallographic specimen and the silver diffraction peaks used as reference data. The respective peaks were determined as the diffractometer was driven both to higher and to lower angles.

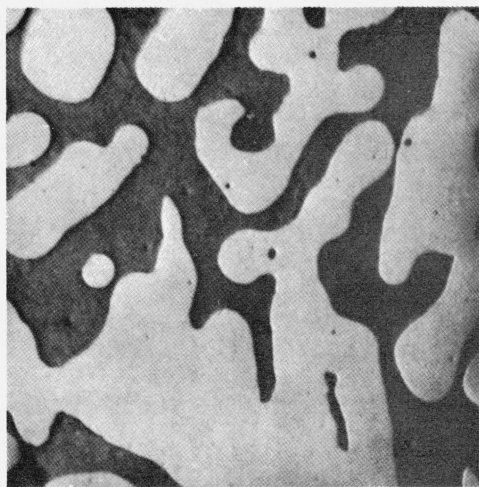
The solid solubility of uranium in ruthenium is about one atomic percent at 1800 °C. The metallographic specimens of the highest ruthenium content appeared to be single phase, while the 97.5 a/o ruthenium alloy had some precipitate phase. The x-ray diffraction results were not conclusive, because the



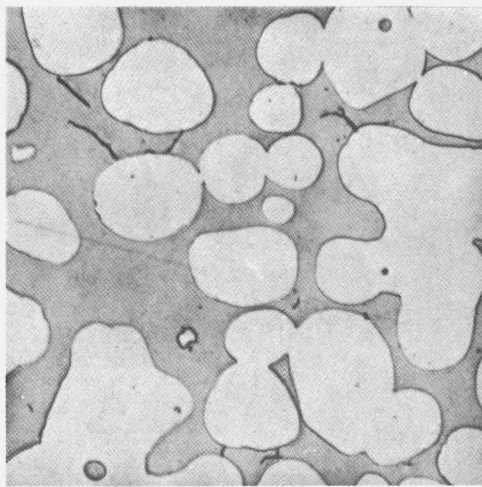
(a)



(b)



(c)



(d)

FIGURE 5

- (a) Alloy of 69.1 a/o ruthenium after thermal analysis, with  $\text{URu}_3$  (white) and  $\text{U}_3\text{Ru}_5$  (grey). Orthophosphoric etch.  $\times 100$ .  
 (b) Alloy of 69.1 a/o ruthenium quenched from 1170 °C, with  $\text{URu}_3$  (white) and  $\text{U}_3\text{Ru}_5$  (grey). Polished.  $\times 100$ .  
 (c) Alloy of 69.1 a/o ruthenium after 90 hrs at 890 °C, with  $\text{URu}_3$  (white) and  $\text{U}_3\text{Ru}_5$  (grey). Perchloric acid etch.  $\times 100$ .  
 (d) Alloy of 70.5 a/o ruthenium after thermal analysis, with  $\text{URu}_3$  (white) and  $\text{U}_3\text{Ru}_5$  (grey). Orthophosphoric etch.  $\times 100$ .



high-angle ruthenium peaks from the 99.2 and 99.7 a/o ruthenium alloys gave identical lattice spacings for a slightly enlarged ruthenium structure, while the similar peaks from the 97.3 and 95.6 a/o ruthenium alloys also gave identical lattice spacings. Extrapolation of the respective lines connecting the data for 0.0, 0.8, and 2.5 a/o and higher uranium content indicated that the uranium solid solubility in ruthenium is very close to 1.3 a/o.

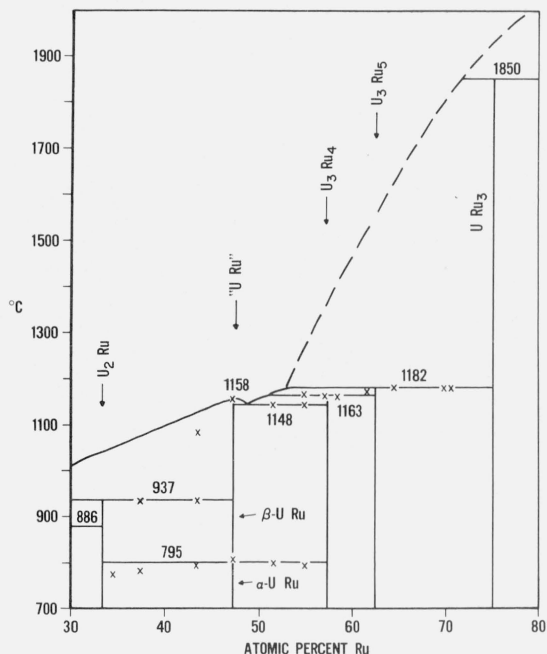


FIGURE 6. The uranium-ruthenium system from 30 to 80 a/o ruthenium.

## 6. Summary of the Uranium-Ruthenium System

The uranium-ruthenium system (fig. 7) is characterized by the existence of five intermetallic compounds. The  $U_2Ru$  phase is formed by a peritectic reaction at 937 °C. The "URu" phase is a congruently melting compound, with a melting point of 1158 °C and with a solid-state transition occurring at 795 °C. The  $U_3Ru_4$  phase is formed peritectically near 1163 °C and it reacts with URu to form a eutectic mixture which melts near 1148 °C. The  $U_3Ru_5$  phase is formed peritectically near 1182 °C. The  $URu_3$  phase also is formed by a peritectic reaction at about 1850 °C. Each of these compounds is stable to room temperature.

A eutectic reaction occurs near the uranium end of the diagram, formed between uranium and the  $U_2Ru$  phase at 886 °C and a composition of about 18.5 a/o ruthenium. The maximum solid solubility of ruthenium in gamma-uranium is about 7.5 a/o, in beta-uranium is near 2 a/o, and in alpha-uranium is less than 1.1 a/o. The maximum solid solubility of uranium in ruthenium is near 1.3 a/o.

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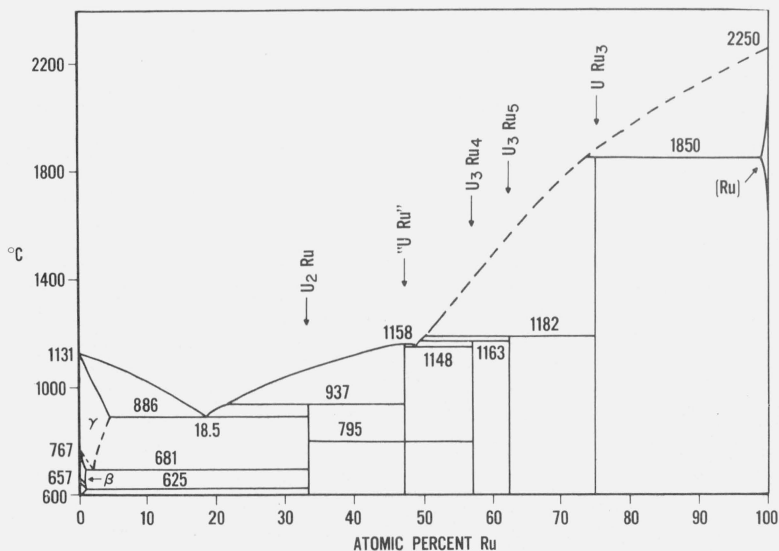


FIGURE 7. The uranium-ruthenium system.

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(Paper 72A1-476)